

U.S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE		DATE: September 26, 2001
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. PCT/N (if known): 09/926228
INTERNATIONAL APPLICATION NO.: PCT/JP00/01669	INTERNATIONAL FILING DATE: MARCH 17, 2000	PRIORITY DATE CLAIMED: MARCH 26, 1999
TITLE OF INVENTION: SELECTIVE REDUCTION TYPE HIGH TEMPERATURE SUPERCONDUCTOR AND METHODS OF MAKING THE SAME		
APPLICANT(S) FOR DO/EO/US: Hideo IHARA		
Applicant hereby submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the time limit set in 35 USC 371(b) and PCT Articles 22 and 39(1).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)): <ul style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) </p> <p>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ul style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. </p> <p>8. <input checked="" type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input checked="" type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>		
ITEMS 11. TO 16. BELOW CONCERN OTHER DOCUMENT(S) OR INFORMATION INCLUDED:		
<p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. ASSIGNEES NAMES AND ADDRESSES: (1) JAPAN SCIENCE AND TECHNOLOGY CORPORATION, Kawaguchi-shi, Japan; and (2) NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY, Tokyo, Japan Please publish the assignee data with the application.</p>		
<p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information: 9 sheets of drawings and international search report.</p>		

U.S. APPLICATION NO. (if known) 09/926228	INTERNATIONAL APPLICATION NO. PCT/JP00/01669	DATE: September 26, 2001	
17. <input checked="" type="checkbox"/> The following fees are submitted:		<u>CALCULATIONS</u>	<u>PTO USE ONLY</u>
Basic National Fee (37 CFR 1.492(a)(1)-(5): Search Report has been prepared by the EPO or JPO: \$860.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$710.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1000.00 International preliminary examination fee (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$100.00			
ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 860.00			
Surcharge of \$130.00 for furnishing the oath or declaration later than <u>20</u> <u>30</u> months from the earliest claimed priority date (37 DVR 1.492(e)).			
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
TOTAL	34 -20 =	14	X \$ 18.00 \$ 252.00
INDEPENDENT	3 - 3 =		X \$ 80.00
Multiple dependent claims(s) (if applicable)		+ \$270.00	\$ 270.00
TOTAL OF ABOVE CALCULATIONS =		\$1,382.00	
Reduction by 1/2 for filing by small entity, if applicable. (Note 37 CFR 1.9, 1.27, 1.28).			
SUBTOTAL =		\$1,382.00	
Processing fee of \$130.00 for furnishing the English translation later than <u>20</u> <u>30</u> months from the earliest claimed priority date (37 CFR 1.492(f)). +			
TOTAL NATIONAL FEE =		\$1,382.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +		\$ 40.00	
TOTAL FEES ENCLOSED =		\$ 1,422.00	
		Amount to be: refunded _____	\$ _____
		charged _____	\$ _____

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- a. A check in the amount of \$1,422.00 to cover the above fees is enclosed. (\$860.00 for basic filing fee; \$252.00 for 14 additional claims; \$270.00 for multiple dependent claims and \$40.00 for Assignment Recordation fee). (This paper is filed in triplicate)
- b. Please charge my Deposit Account No. 01-2340 in the amount of \$____ to cover the above fees. (A duplicate copy of this sheet is enclosed.)
- c. The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-2340.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed to request that the application be restored to pending status.

Send All Correspondence To:



23850

PATENT TRADEMARK OFFICE

SIGNATURE

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NAME

32,878

REGISTRATION NUMBER

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PATENT
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: **Hideo IHARA**

Serial No.: **Not Yet Assigned**
(PCT/JP00/01669)

Filed: **September 26, 2001**

For: **SELECTIVE REDUCTION TYPE HIGH TEMPERATURE SUPERCONDUCTOR
AND METHODS OF MAKING THE SAME**

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

September 26, 2001

Sir:

Prior to the calculation of the filing fees of the above application, please amend the application as follows:

IN THE SPECIFICATION:

Please replace the paragraph beginning at page 10, line 10, with the following rewritten paragraph:

A selective reduction method of the present invention is a method whereby polyvalent, reducible ions (e.g., Tl ion) substituted for a portion of Cu ions in the charge supply layers of a high temperature superconductor are reduced (their ionic valence is reduced) by decreasing the oxygen content in the high temperature superconductor (e.g., by heat treatment in a reducing atmosphere). It is by this reduction of reducible substituted ions that the electronic and band structures of a Cu-oxide high temperature superconductor vary and a mechanism is revealed that permits doping with positive holes. It should also be noted at this point that term "selective reduction type high temperature superconductor", as used herein, of the present invention is intended to refer to a high

temperature superconductor that comprises a pair of charge supply layers constituted by an upper and a lower surface of a unit superconductor lattice having each of a portion of Cu atoms in these surfaces substituted with polyvalent, reducible ions and having these substitutional ions exclusively and selectively reduced, and a superconducting layer as a layer other than those upper and lower surfaces.

IN THE CLAIMS:

Please cancel claims 1-21 without prejudice or disclaimer and add new claims 22-44 as follows:

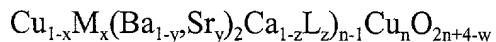
22. A selective reduction type high temperature superconductor, characterized in that the high temperature superconductor has a unit cell that comprises a pair of charge supply layers formed by an upper and a lower surface thereof having each of a portion of Cu atoms substituted with a selectively reducible atom, and superconducting layers as layers other than said charge supply layers, wherein said charge supply layers have said selectively reduced atoms selectively reduced.

23. A selective reduction type high temperature superconductor as set forth in claim 23, characterized in that selective reduction as aforesaid of said high temperature superconductor forms in said superconducting layers of the high temperature superconductor a first and a second region which are doped overly and doped optimally, respectively, with superconducting carriers.

24. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that selective reduction as aforesaid of said high temperature superconductor maintains a superconducting carrier concentration in said superconducting layers in toto as doped overly or as doped optimally with the superconducting carriers.

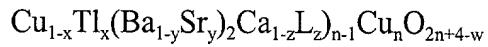
25. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that said superconducting layers of said high temperature superconductor have an upper and a lower surface constituted by a CuO₂ surface of 5-coordination and a surface other than the upper and lower constituted by a CuO₂ surface of 4-coordination.

26. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that it is made of a (Cu, M) family high temperature superconducting material that can be described by composition formula:



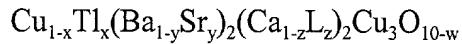
where M represents ions of one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os; L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

27. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that it is made of a (Cu, Tl) family high temperature superconducting material that can be described by composition formula:



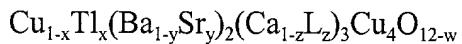
where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

28. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that it is made of a (Cu, Ti) family high temperature superconducting material that can be described by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

29. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that it is made of a high temperature superconducting material that can be described by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

30. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that the concentration of superconducting carriers is adjusted by selective reduction or by varying (increasing or decreasing) oxygen concentration.

31. A selective reduction type high temperature superconductor as set forth in claim 26, characterized in that it is a selectively over-doped type or a selectively optimum-doped type, high temperature superconductor in which n is any one of 3, 4, 5, 6 and 7.

32. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that selective reduction causes said substitutional atoms in a said charge supply layer to receive electrons in their outer shell orbits, thereby providing holes in the CuO₂ surface of 5-coordination of a said superconducting layer.

33. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that it has a superconducting anisotropy of not greater than 10, and a coherence distance of not less than 3 angstroms.

34. A selective reduction type high temperature superconductor as set forth in claim 22 or claim 23, characterized in that said selective reduction transforms its natural superconducting wave function that is of a d-wave to a wave function of a (d + is) wave that has also a property of an s-wave.

35. A method of making a selective reduction type high temperature superconductor, characterized in that it comprises the steps of:

adding an element exhibiting a self-assembling effect and selective reducibility to a raw material of a high temperature superconductor;

using the self-assembling effect of said element to cause a crystal of the high temperature superconductor to grow with a structure in which said element is substituted for a portion of Cu atoms in a charge supply layer of a basic cell of the high temperature superconductor; and

using the selective reducibility of said element to selectively reduce said element in the charge supply layer of the basic cell of said high temperature superconductor crystal.

36. A method of making a selective reduction type high temperature superconductor as set forth in claim 35, characterized in that:

the step of causing the high temperature superconductor crystal to grow includes the steps of admixing together a precursor of the high temperature superconductor, a chemical compound of said element and a oxidizing and a reducing agent to form a mixture thereof, and heat treating said mixture in a high pressure condition; and

the step of selective reduction comprises heat treating said high temperature superconductor crystal in a reducing atmosphere.

37. A method of making a selective reduction type high temperature superconductor as set forth in claim 36, characterized in that:

said mixture comprises a mixture formed by admixing said precursor represented by composition formula: $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$, said element chemical composition constituted by Ti_2O_3 , said oxidizing agent constituted by AgO or CaO_2 and said reducing agent constituted by Cu_2O with a prepared composition: $\text{Cu}_{0.5}\text{Ti}_{0.5}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$;

the step of causing said high temperature superconductor to crystallographically grow includes a heat treatment under a high pressure of 5Gpa at a temperature of 850°C for a period of 2 hours; and

the step of selective reduction includes a heat treatment at a temperature of 400 to 700°C, preferably at 540°C, for a period of 12 hours in a reducing atmosphere in N₂;

thereby forming a selective reduction type high temperature superconductor having a Cu-1223 structure and represented by composition formula: (Cu_{1-x}Tl_x)Ba₂Ca₂Cu₃O_y where 0≤x≤1.0 and 0≤y≤1.

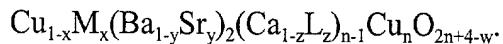
38. A method of making a selective reduction type high temperature superconductor as set forth in claim 36, characterized in that:

the precursor of said high temperature superconductor is a precursor represented by composition formula:

Cu(Ba_{1-y}Sr_y)₂(Ca_{1-z}L_z)_{n-1}Cu_nO_{2n+4-w} where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; 0≤x≤1.0; 0≤y≤1; 0≤z≤1; 0≤w≤4; and 1≤n≤16; and

the chemical compound of said element exhibiting said self-assembling effect and said selective reducibility is a compound containing one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os;

thereby forming a selective reduction type high temperature superconductor having a Cu-1223 structure and represented by composition formula:



39. A method of making a selective reduction type high temperature superconductor, characterized in that it comprises the steps of:

heat treating in an atmosphere of an element exhibiting a self-assembling effect and a selective reducibility an amorphous film of a high temperature superconductor composition containing said element deposited on a single crystalline substrate;

using the self-assembling effect of said element and an epitaxy effect of said single crystalline substrate to cause a high temperature superconductor to crystallographically grow with a structure having said element substituted for a portion of Cu atoms in a charge supply layer of a basic cell of the high temperature superconductor; and

using the selective reducibility of said element to selectively reduce said element in the charge supply layer of the basic cell of said high temperature superconductor.

40. A method of making a selective reduction type high temperature superconductor as set forth in claim 39, characterized in that:

the step of causing said high temperature superconductor to crystallographically grow includes the steps of preparing a mixture pellet containing said element and a pellet for adjusting the concentration of said element, depositing said amorphous film on said single crystalline substrate by spattering a target of a high temperature superconductor composition containing said element, and heat treating said mixture pellet, said concentration adjustment pellet and said amorphous film commonly in a closed container; and

the step of selective reduction includes heat treating said high temperature superconductor crystal in a reducing atmosphere.

41. A method of making a selective reduction type high temperature superconductor as set forth in claim 40, characterized in that:

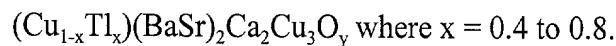
 said mixture pellet is a mixture of a high temperature superconductor precursor whose constituent elements are Cu, Ba, Ca and O with Tl_2O_3 as a chemical compound of said self-assembling effect and selective reducibility exhibiting element in a composition range expressed by composition formula: $Cu_{1-x}Tl_xBa_2Ca_3Cu_4O_y$ where $x = 0.25$ to 0.5 and formed by pressing;

 said concentration adjustment pellet is a thallium concentration adjustment pellet formed by heat treating a said mixture pellet for a period of 1 hour;

 said amorphous film is obtained by spattering a sintered target of a composition expressed by composition formula: $TlBaSrCa_2Cu_3O_y$ to deposit the composition on a $SrTiO_3$ substrate; the heat treatment in said closed container is performed at a temperature of 860 to 900 for a period of 30 to 90 minutes;

 the step of selective reduction include a heat treatment effected at a temperature of $500^\circ C$ for a period of 30 minutes in a reducing atmosphere of low pressure oxygen gas at a pressure not in excess of 1 atm; and

 thereby forming a selective reduction type high temperature superconductor having a Cu-1223 structure and expressed by composition formula:



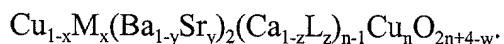
42. A method of making a selective reduction type high temperature superconductor as set forth in claim 40, characterized in that:

 said mixture pellet is a mixture of a high temperature superconductor precursor whose constituent elements are Cu, Ba, Ca and O with a chemical compound containing one or more of self-assembling effect and selective reducibility exhibiting elements as aforesaid M selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os in a composition range expressed by composition formula: $Cu_{1-x}M_xBa_2Ca_3Cu_4O_y$ where $x = 0.25$ to 0.5 and formed by pressing;

 said concentration adjustment pellet comprises an M concentration adjustment pellet formed by heat treating a said mixture pellet for a period of 1 hour;

 said target is a sintered target of a composition expressed by composition formula: $TlBaSrCa_2Cu_3O_y$; and

 thereby forming a (Cu, M) family, selective reduction type high temperature superconductor having a Cu-1223 structure and expressed by composition formula:



43. A method of making a selective reduction type high temperature superconductor as set forth in claim 40, characterized in that:

 said mixture pellet is a mixture of a high temperature superconductor precursor whose constituent elements are Cu, Ba, Ca and O with Tl_2O_3 as a chemical compound of said self-assembling effect and selective reducibility exhibiting element in a composition range expressed by composition formula: $Cu_{1-x}Tl_xBa_2Ca_3Cu_4O_y$ where $x = 0.25$ to 0.5 and formed by pressing;

said concentration adjustment pellet is a thallium concentration adjustment pellet formed by heat treating a said mixture pellet for a period of 1 hour;

said amorphous film is obtained by spattering a sintered target of a composition expressed by composition formula: $Cu_{1-x}Tl_xBa_2Ca_3Cu_4O_y$ to deposit the composition on a $SrTiO_3$ substrate; the heat treatment in said closed container is performed at a temperature of 880 to 920°C for a period of 60 minutes;

the step of selective reduction include a heat treatment effected at a temperature of 450 to 500°C for a period of 30 minutes in a reducing atmosphere of low pressure oxygen gas at a pressure not in excess of 1 atm; and

thereby forming a selective reduction type high temperature superconductor having a Cu-1234 structure and expressed by composition formula: $Cu_{1-x}Tl_xBa_2Ca_3Cu_4O_y$.

44. A method of making a selective reduction type high temperature superconductor as set forth in claim 40, characterized in that:

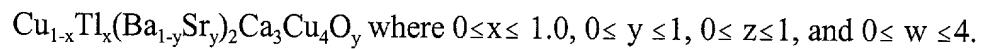
said mixture pellet is a mixture of a high temperature superconductor precursor whose constituent elements are Cu, Ba, Ca and O with Tl_2O_3 as a chemical compound of said self-assembling effect and selective reducibility exhibiting element in a composition range expressed by composition formula: $Cu_{1-x}Tl_xBa_2Ca_3Cu_4O_y$ where $x = 0.25$ to 0.5 and formed by pressing;

said concentration adjustment pellet is a thallium concentration adjustment pellet formed by heat treating a said mixture pellet for a period of 1 hour;

said amorphous film is obtained by spattering a sintered target of a composition expressed by composition formula: $Cu_{1-x}Tl_x(Ba_{1-y}Sr_y)_2(Ca_{1-z}L_z)_3Cu_4O_{12-w}$ to deposit the composition on a $SrTiO_3$

substrate; and

thereby forming a selective reduction type high temperature superconductor having a Cu-1234 structure and expressed by composition formula:



REMARKS

Claims 22-44 are pending. Claims 1-21 have been cancelled. New claims 22-44 substantially correspond to the claims after entry of the amendments under Articles 19 and 34, while also correcting improper multiple dependent claims.

The above amendment is believed to place the claims in proper condition for examination.

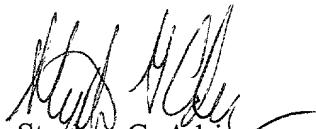
Early and favorable action is awaited.

Attached hereto is a marked-up version of the changes made to the specification by the current amendment. The attached page is captioned "Version with markings to show changes made."

In the event there are any additional fees required, please charge our Deposit Account No. 01-2340.

Respectfully submitted,

ARMSTRONG, WESTERMAN, HATTORI,
McLELAND & NAUGHTON, LLP



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SGA/yap

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

The paragraph beginning at page 10, line 10, has been amended as follows:

A selective reduction method of the present invention is a method whereby polyvalent, reducible ions (e.g., Tl ion) substituted for a portion of Cu ions in the charge supply layers of a high temperature superconductor are reduced (their ionic valence is reduced) by decreasing the oxygen content in the high temperature superconductor (e.g., by heat treatment in a reducing atmosphere). It is by this reduction of reducible substituted ions that the electronic and band structures of a Cu-oxide high temperature superconductor vary and a mechanism is revealed that permits doping with positive holes. It should also be noted at this point that term “selective reduction type high temperature superconductor” as used herein, of the present invention is intended to refer to a high temperature superconductor that comprises a pair of charge supply layers constituted by an upper and a lower surface of a unit superconductor lattice having each of a portion of Cu atoms in these surfaces substituted with polyvalent, reducible ions and having these substitutional ions exclusively and selectively reduced, and a superconducting layer as a layer other than those upper and lower surfaces.

3/Pr/s

SPECIFICATION

SELECTIVE REDUCTION TYPE HIGH TEMPERATURE SUPERCONDUCTOR AND METHODS OF MAKING THE SAME

5

Technical Field

This invention relates to a selective reduction type high temperature superconductor, which is a copper (Cu) oxide high temperature superconductor that permits doping with positive holes by 10 selectively reducing constituent elements (atoms), which superconductor can be used in large scale superconducting power transmission, superconducting power storage or reserve, superconducting electronics such as a high performance Josephson device, a high frequency device or the like. The invention also relates 15 to methods of making such a superconductor.

Background Art

Conventional Cu-oxide family high temperature superconductors have been prepared doped with positive holes, by oxidation, to raise the 20 contents of the superconducting carriers. Such a high temperature superconductor, however, may have the carriers reduced in concentration due to diffusion or bleeding of oxygen atoms by temperature rise. This lead to a depletion in superconductivity of the superconductor.

25 Also, doping with positive holes to obtain a higher carrier concentration has been thought to require a higher oxygen partial pressure, and it has so fare been unattainable to prepare a superconductor of the type described by doping with positive holes to raise the carrier concentration in a reduction process conditioned under 30 low partial pressure or vacuum. Thus, it having been found impossible to increase the concentration of positive holes by reduction, i.e., by lowering the oxygen concentration, the conventional high temperature

superconductors have had the problem to be resolved that they when prepared in the reducing atmosphere of a reduced oxygen pressure have a limited carrier concentration and are thus low and unsatisfactory in their superconducting properties that include the critical temperature 5 T_c , critical current density J_c , irreversible magnetic field H_{irr} . It has therefore been sought to solve the problem of bringing into realization a high temperature superconductor of a reduced oxygen concentration.

With these problems taken into account, it is accordingly a first object of the present invention to provide a selective reduction type 10 high temperature superconductor that permits doping with positive holes by selectively reducing constituent elements (atoms).

Another object of the present invention is to provide a method of making a selective reduction type high temperature superconductor.

15 Summary of the Invention

In order to achieve the first object mentioned above, there is provided in accordance with the present invention, a selective reduction, high temperature superconductor, wherein it has a portion of its constituent elements selectively reduced whereby it has a 20 superconducting layer thereof doped with positive holes.

The present invention also provides a selective reduction type high temperature superconductor that has a portion of its constituent elements selectively reduced whereby there are formed in superconducting layers a first and a second region doped overly and 25 doped optimally with superconducting carriers, respectively.

The present invention further provides a selective reduction type high temperature superconductor that has a portion of its constituent elements selectively reduced whereby the superconductor as a whole has a superconducting carrier concentration such that it is 30 held doped overly or doped optimally with superconducting carriers.

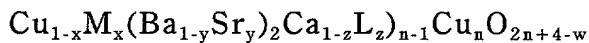
The present invention also provides a selective reduction type high temperature superconductor that has on each of an upper and a

lower surface of a unit lattice thereof a charge supply layer having each of a portion of Cu atoms substituted with a selectively reducible atom.

The present invention also provides a selective reduction type high temperature superconductor in which the said superconducting 5 layers have an upper and a lower surface constituted by a CuO₂ surface of 5-coordination and a surface other than the upper and lower constituted by a CuO₂ surface of 4-coordination, the said CuO₂ surfaces of 5-coordination and 4-coordination having been over- and optimum-doped, respectively, by selective reduction.

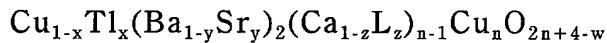
10 Further, the present invention provides a selective reduction type high temperature superconductor having a selectively over-doped and/or a selectively optimum-doped construction.

The present invention further provides a selective reduction type high temperature superconductor, characterized in that it is made 15 of a (Cu, M) family high temperature superconducting material, which can be described by composition formula:



where M represents ions of one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, 20 Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os; L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

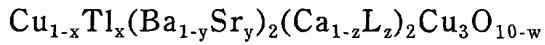
The present invention also provides selective reduction type 25 high temperature superconductor, characterized in that it is made of a (Cu, Tl) family high temperature superconducting material that can be described by composition formula:



where L represents one or more elements selected from the class which 30 consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

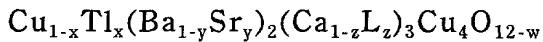
The present invention also provides a selective reduction type

high temperature superconductor, characterized in that it is made of a (Cu, Tl) family high temperature superconducting material that can be described by composition formula:



5 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

10 The present invention also provides a selective reduction type high temperature superconductor, characterized in that it is made of a high temperature superconducting material that can be described by composition formula:



15 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

20 The present invention further provides a selective reduction type high temperature superconductor, characterized in that selective over- or optimum-doping is effected by decrease in the valence number of ions of a constituent element by decrease in the oxygen concentration, that is by selective reduction, or by varying (increasing or decreasing) oxygen concentration.

25 The present invention also provides a selective reduction type high temperature superconductor, characterized in that it is a selectively over-doped type or a selectively optimum-doped type high temperature superconductor in which n is any one of 3, 4, 5, 6 and 7.

30 The present invention further provides a selective reduction type high temperature superconductor having a construction that the reduction of selectively reducible ions causes the ions in the charge supply layers to receive electrons in their outer shell orbits, thereby providing holes in the CuO_2 surface of 5-coordination of a said superconducting layer.

The present invention further provides a selective reduction

type high temperature superconductor having a construction that it has a superconducting anisotropy of not greater than 10 and a coherence distance of not less than 3 angstroms.

The present invention further provides a selective reduction
5 type high temperature superconductor having a construction that said selective reduction transforms its natural superconducting wave function that is of a d-wave high in spatial anisotropy to a wave function of a (d + is) wave that has also a property of an s-wave lacking of spatial anisotropy.

10 A selective reduction type high temperature superconductor so constructed as mentioned above according to the present invention can be prepared in a reducing atmosphere or can in use have its oxygen content decreased, still to maintain its critical temperature T_c high, while providing a reduced superconductivity γ , a high critical current density J_c and a high irreversibility field H_{irr} .
15

Stated otherwise, a selective reduction type high temperature superconductor according to the present invention is provided with a crystalline and an electronic structure that permits achieving improved J_c and H_{irr} while maintaining T_c high. Moreover, provided with a
20 superconducting wave function of a (d + is) wave, it is low in superconducting anisotropy. With these advantages, it can be used as a high performance, high temperature superconductor in a variety of industrial sub-fields concerned.

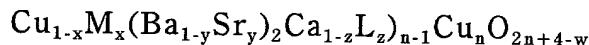
In order to achieve the second object mentioned above, the
25 present invention provides a method of making a selective reduction type high temperature superconductor, which comprises the steps of: preparing a high temperature superconductor, and heat-treating the prepared high temperature superconductor in a reducing atmosphere.

The present invention also provides a method of making a
30 selective reduction type high temperature superconductor, comprising the steps of: using an amorphous film as a precursor of high temperature superconductor; causing the amorphous film to grow

epitaxially by amorphous phase epitaxy; and heat-treating in a low oxygen, reducing atmosphere the amorphous film that has grown epitaxially.

The present invention further provides a method of making a
5 selective reduction type high temperature superconductor, comprising
the steps of: causing added constituent elements to develop their self-
assembling (or self-forming) effect; and causing the high temperature
superconductor to grow epitaxially by the self-assembling effect.

A method of making a selective reduction type high
10 temperature superconductor of the present invention as mentioned
above is applicable to making a (Cu, M) family selective reduction type
high temperature superconductor expressed by composition formula:



where M represents ions of one or more polyvalent metallic elements
15 selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr,
Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os; L represents one or more
elements selected from the class which consists of Mg and alkaline
metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

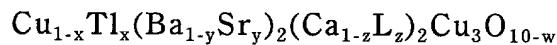
20 A method of making a selective reduction type high
temperature superconductor of the present invention as mentioned
above is also applicable to making a (Cu, Tl) family selective reduction
type high temperature superconductor expressed by composition
formula:



where L represents one or more elements selected from the class which
consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

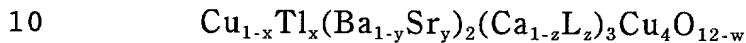
30 A method of making a selective reduction type high
temperature superconductor of the present invention as mentioned
above is also applicable to making a (Cu, Tl) family selective reduction
type high temperature superconductor expressed by composition

formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

A method of making a selective reduction type high temperature superconductor of the present invention as mentioned above is also applicable to making a selective reduction type high temperature superconductor expressed by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

15 A method of making a selective reduction type high temperature superconductor of the present invention so constructed as mentioned above permits manufacturing a positive hole dopable or doped selective reduction type high temperature superconductor.

Brief Description of the Drawings

20 The present invention will better be understood from the following detailed description and the drawings attached hereto showing certain illustrative forms of embodiment of the present invention. In this connection, it should be noted that such forms of embodiment illustrated in the accompanying drawings hereof are 25 intended in no way to limit the present invention but to facilitate an explanation and understanding thereof.

In the drawings:

Fig. 1 is a diagram showing modeled crystal structures of a selective reduction type high temperature superconductor according to 30 the present invention in which (a) and (b) show unit cells with $n = 1$ and $n = 2$, respectively;

Fig. 2 is a diagram showing modeled crystalline structures of a

selective reduction type high temperature superconductor according to the present invention in which (a), (b) and (c) show unit cells with $n = 3$, $n = 4$ and $n = 5$, respectively;

Fig. 3 is a diagram showing the temperature dependency of the electrical resistivity according to a first form of embodiment of the present invention annealed at various temperatures in a nitrogen atmosphere;

Fig. 4 is a diagram showing thermo-analysis data according to the first form of embodiment of the invention;

Fig. 5 is a diagram showing change of the hole concentration with temperature according to the first form of embodiment of the invention annealed in nitrogen atmosphere;

Fig. 6 is a diagram showing relationships between T_c , normal conduction electrical resistivity, carrier concentration, weight's rate of change of, and annealing temperature for, specimens according to the first form of the invention annealed in nitrogen atmosphere;

Fig. 7 is a diagram showing an electronic state according to the first form of embodiment of the invention that is high in oxygen concentration;

Fig. 8 is a diagram showing an electronic state according to the first form of embodiment of the invention that is low in oxygen concentration; and

Fig. 9 is a diagram showing an X-ray diffraction analysis pattern according to a second form of embodiment of the present invention.

25

Best Modes for Carrying Out the Invention

Hereinafter, the present invention for a selective reduction type high temperature superconductor and a method of its making will be described in detail with respect to suitable forms of embodiment thereof illustrated in Figs. 1 to 9.

While the conventional methods for increasing the carrier concentration in a high temperature superconductor rely either on

oxidation by heat treatment in high pressure oxygen or on substitution to form elements of varying valence numbers, a selective reduction type high temperature superconductor according to the present invention is characterized in that it has an increased concentration of 5 positive holes achieved by reduction, namely by lowering the oxygen concentration, which permits enhancing its T_c (critical temperature), J_c (critical current density) and H_{irr} (high irreversibility field) to a considerable extent.

A Cu-oxide super conductor of the present invention:

10 $Cu_{1-x}M_x(Ba_{1-y}Sr_y)_2(Ca_{1-z}L_z)_{n-1}Cu_nO_{2n+4-w}$
includes charge supply layers formed by $Cu_{1-x}M_x$ surfaces that make up the upper and lower surfaces of a unit cell, and superconducting layers that make up the other surfaces (surfaces other than the upper and lower) of the unit cell, namely those formed by CuO_2 surfaces of a 15 pyramidal CuO_5 cluster, i.e., CuO_2 surfaces of 5-coordination and those formed by CuO_2 surfaces of a planar CuO_4 cluster, i.e., CuO_2 surfaces of 4-coordination, these different superconducting layers being laid alternately one on another.

20 Figs. 1 and 2 illustrate modeled crystal structures of selective reduction type high temperature superconductors of the present invention. These modeled crystal structures are illustrated for a $CuBaCa_{n-1}O_{2n+4-w}$ where $1 \leq n \leq 16$ and $0 \leq w \leq 4$, in particular with respect to examples thereof in which n is an integer from 1 to 5.

25 Fig. 1(a) is for a unit cell where n is 1, and Fig. 1(b) is for a unit lattice where n is 2. In Fig. 2, (a), (b) and (c) are for unit cells where n is 3, 4 and 5, respectively.

30 Referring to Fig. 2(a), a selective reduction type high temperature superconductor of the present invention comprises a pair of $Cu_{1-x}M_x$ surfaces 1, 1 that constitute its charge supply layers, a CuO_2 surface 2 of 5-coordination that constitutes a superconducting layer and a CuO_2 surface 3 of 4-coordination that constitutes a superconducting layer.

According to a selective reduction method of the present invention, a superconducting layer is formed as a CuO_2 surface 2 of 5-coordination in which the density of positive holes is such that it is either overly (excessively) or optimally doped with them, or nearly so 5 doped, and is formed as a CuO_2 surface 3 of 4-coordination in which the density of positive holes is such that it is optimally or nearly optimally doped with them. To wit, the method permits forming an excessively or optimally doped CuO_2 surface and an optimally doped CuO_2 surface selectively and separately.

10 A selective reduction method of the present invention is a method whereby polyvalent, reducible ions (e.g., Tl ion) substituted for a portion of Cu ions in the charge supply layers of a high temperature superconductor are reduced (their ionic valence is reduced) by decreasing the oxygen content in the high temperature superconductor 15 (e.g., by heat treatment in a reducing atmosphere). It is by this reduction of reducible substituted ions that the electronic and band structures of a Cu-oxide high temperature superconductor vary and a mechanism is revealed that permits doping with positive holes.

Fig. 7 is a diagram that shows an electronic state of the CuO_2 , 20 surface 2 of an afore-mentioned Cu-oxide high temperature superconductor in case its oxygen concentration is high, and Fig. 8 is a diagram that shows an electronic state of the CuO_2 surface 2 of an afore-mentioned Cu-oxide high temperature superconductor in case its oxygen concentration is decreased.

25 Referring to Figs. 7 and 8, if the oxygen concentration is high it is seen that Tl ions present in a charge supply layer is in a plus (+) trivalent state and the Tl6s level is above the Fermi level. If as a result of oxygen reduction the oxygen concentration is lowered, Tl ions take a plus monovalent state and the Tl6s level lies below the Fermi level.

30 As a consequence, electrons are pulled out of the CuO_2 surface of 5-coordination as a superconducting layer and holes are supplied into the CuO_2 surface of 5-coordinate, the superconducting layer. In this way,

reducing reducible polyvalent ions such as Tl ions by decreasing the oxygen concentration, namely supplying positive holes by selective reduction permits increasing the carrier concentration. In the context hereof, supplying positive holes by selective reduction is referred to as
5 selective doping.

Using selective doping enables producing a high performance, high temperature superconductor. For example, heat-treating in a reducing atmosphere such a high temperature superconductor formed in an overly doping composition to decrease oxygen by a certain amount
10 decreases the carrier concentration because of the superconducting layers losing oxygen, but permits the CuO₂ surface 2 of coordination number 5 as one superconducting layer to stay in an overly doped state by being injected with holes by selective doping.

On the other hand, the 4-coordination CuO₂ surface 3 providing
15 for the other superconducting layer is not doped with holes and therefore has a reduced carrier concentration, staying in an optimally doped state. Thus, a makeup is provided in which while the superconducting layers as a whole are overly doped, there also exists an optically doped CuO₂ surface. The method mentioned above is referred
20 to herein as selective over-doping method. Likewise, it is also possible to make both the 5-coordination and 4-coordination CuO₂ surface superconducting layers doped optimally in their carrier concentration. This alternative method is referred to herein as selective optimum doping method.

25 A difference in potential level between more than one types of CuO₂ surfaces and a difference in energy level between the bands which these CuO₂ surfaces possess can be used in this manner to permit the over-doped CuO₂ surface and the optimum-doped to coexist in a unit cell, and thus to have T_c, J_c and H_{irr} of the superconductor raised
30 considerably.

By the way, T_c varies with respect to the amount of doping, parabolically or along a parabolic curve opening downwards, whereon

the optimum doping is established at the amount of doping at which T_c becomes maximum. In the case of Cu-oxide high temperature superconductors, this corresponds to the number of holes for one Cu (atom) that is 0.2 to 0.23. Further, over-doping indicates the amount of 5 doping that is greater than that for optimum doping. Using the selective over-doping method according to the present invention gives rise to over-doping as a whole and thus large J_c , but by the presence of an optimum-doped superconducting layer as mentioned above does not lower T_c despite over-doping.

10 Thus, in a Cu-oxide selective reduction type high temperature superconductor of the present invention, use is made of a change in the electronic and band structures formed by substitution of polyvalent reducible ions, e.g., Tl ions, for a portion of Cu ions in the charge supply layers to realize a mechanism that permits selective doping with 15 positive holes.

20 This mechanism in a selective reduction type high temperature superconductor of the present invention despite shortage of oxygen in the superconducting layers or against the inability to enough supply them with oxygen in the preparation step of the superconductor causes 25 the substitute ions to pull electrons out of the superconducting layers and thus to supply them with positive holes. Accordingly, there results here no deterioration in properties as does if oxygen comes off, and then the preparation in an atmosphere of low oxygen partial pressure still permits yielding a high temperature superconductor of high 25 performance.

Further, given the superconducting layers formed in an over-doped state as suitably composed and structured, the use of this mechanism whereby selective doping by selective reduction permits the 5-coordination CuO_2 surface to stay over-doped while rendering the 4-30 coordination CuO_2 surface optimum-doped makes it possible to raise J_c while at the same time holding T_c high. In this case, the superconducting layers may, as suitably composed and structured, be

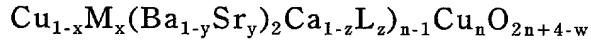
formed also in an optimum-doped state.

While both optimum-doping and over-doping are described above as being controllable by decrease in the valence number of Tl ions by reduction in oxygen content, it is, of course, possible to control them by 5 increase and decrease in oxygen content.

A selective reduction type high temperature superconductor of the present invention as described above can be made first by preparing a high temperature superconductor by using high pressure synthesis, hot pressing, spattering, laser ablation or the like irreversible or non-10 equilibrium process of manufacture, and then by subjecting it to reduction heat-treatment.

The above-mentioned method of making according to the present invention is applicable to making selective reduction type high temperature superconductors as can be described by the composition 15 formula (a) mentioned below.

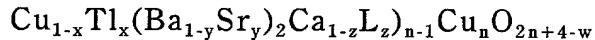
Composition Formula (a):



where M represents ions of one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, 20 Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os; L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

The above-mentioned method of making according to the present 25 invention is further applicable to making selective reduction type high temperature superconductors as can be described by the composition formula (b) mentioned below.

Composition Formula (b):



30 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

In order to prepare thin films of a Cu-oxide superconductor:

$Cu_{1-x}M_x(Ba_{1-y}Sr_y)_2Ca_{1-z}L_z)_{n-1}Cu_nO_{2n+4-w}$ having a layer structure according to the present invention, it is necessary that charge supply layers and superconducting layers be laid one on another alternately.

5 Also required is that each layer be formed under accurate control of its composition and crystallinity and be of a large area.

This in turn requires, in addition to physical control such as for temperature and pressure, that additional element M exhibit its auto-forming capacity and that the crystal periodicity and atomic ordering in
10 the CuO_2 plane and in the direction perpendicular thereto be enhanced to an ideal level. An improvement in the in-plane ordering by the epitaxial effect and an improvement in the crystallinity in the plane and in the direction perpendicular thereto by the chemical auto-formation effect of the additional element M result in a large improvement in the
15 atomic ordering in the thin film crystal, which in turn contributes to a rise in superconductivity. An example of the additional element M is the utilization of $M = Ti$ which possesses the structure stabilizing effect, the reaction accelerating effect, the charge supply effect and the T_c increasing effect together in combination. This additional element M if
20 thin films are prepared properly under control, has been found to exhibit the same or similar effects in forming high temperature superconductors other than those mentioned above. The method of making according to the present invention is designed to utilize the effects described above.

25 It should further be noted that a high temperature superconducting material according to the present invention possesses a d-wave superconductivity by being a material that is large in Coulomb repulsion and of strong correlativity. As a result, it is considerably large in superconducting anisotropy in the CuO_2 plane. This anisotropy
30 can be made smaller by the selective reduction of the present invention. To wit, as shown in Fig. 8, performing the selective reduction brings electrons in the CuO_2 plane into a [d + is] state where an s-wave

property is introduced that is characteristic of a superconducting material of weak correlativity. This leads to realization of a high performance superconducting material that is small in anisotropy.

It is thus seen that the method of making according to the 5 present invention achieves the preceding effect as well.

Mention is next made of a first, preferred form of embodiment of the invention represented by an example having a composition: $(Cu_{1-x}Tl_x)Ba_2Ca_2Cu_3O_y$ where $0 \leq x \leq 1.0$ and $0 \leq y \leq 1$, and having a structure with a unit cell illustrated in Fig. 2(a). The structure of 10 specimen for this first form of embodiment of the invention as indicated in Fig. 2(a) is referred to here as Cu-1223.

An explanation is first given in respect of a method of making this first form of embodiment of the invention.

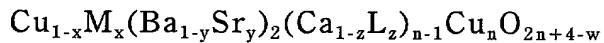
Raw materials to make up a selective reduction type high 15 temperature superconductor as the first form of embodiment of the invention are: CuO, BaCO₃, CaCO₂, BaO₂ and CaO₂ with an oxidizing agent such as of AgO or CaO₂ and a reducing agent such as of Cu₂O.

First, a precursor of Ba₂Ca₂Cu₃O₇ has CuO and Tl₂O₃ mixed therewith in a proper amount, and a specimen having a composition: 20 $(Cu_{1-x}Tl_x)Ba_2Ca_2Cu_3O_y$ ($x = 0.5$) is prepared by synthesis in a cubic anvil high pressure generating apparatus under conditions of 850°C, 5 Gpa and 2 hours.

Next, this specimen is annealed in a reducing atmosphere, e.g., of nitrogen gas, of a temperature range from 400 °C to 700 °C, 25 preferably at 540°C for a period of 12 hours. This selective reduction treatment gives rise to a selective reduction type high temperature superconductor of this form of embodiment of the invention.

What is to be mentioned further is that the above-mentioned method of making according to the present invention is also applicable 30 to making selective reduction type high temperature superconductors as can be described by the composition formula (c) mentioned below.

Composition Formula (c):



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

5 An explanation is next given in respect of properties of the first form of embodiment of the invention.

Fig. 3 is a diagram that indicates the temperature dependency of the electrical resistivity for various temperatures at which annealing is effected in the first form of embodiment.

10 As shown in Fig. 3, T_c rises from 97 K to 131 K as the annealing temperature is raised. The curves' gradient varies somewhat in the vicinity of T_c for the annealing temperatures from 350°C to 450°C, apparently due to uniformity of the specimen. A normal conduction electrical resistivity rises for the annealing temperature that is raised
15 from 200°C to 400°C, and then falls for the annealing temperature of 400°C to 550°C, followed by a rise at the annealing temperature of 600°C.

Fig. 4 is a diagram showing thermo-analysis data in the first form of embodiment of the invention.

20 From the results of the thermo-gravimetric analysis (TG) as shown in Fig. 4, it is shown that the weight decreases as the annealing temperature is raised and especially that it falls sharply in the vicinity of 400°C and in excess of 700°C. From the results of the differential thermal analysis (DTA), it is also seen that the losses in weight near
25 400°C and more than 700°C are each due to emission of oxygen and T_1 .

Fig. 5 is a diagram showing that the hole concentration changes with the temperature in the first form of embodiment of the invention.

As shown in Fig. 5, the carriers for Cu found from measurement of Hall coefficient has a density of 0.5 at the temperature of 300 K for a
30 specimen as it is formed by high pressure synthesis, which leaves the specimen over-doped. However, annealing changes the carrier density. Thus, while annealing at 400°C reduces the carrier density to 0.12 and

brings the specimen into an under-doped state, annealing at 540°C gives rise to a carrier density of 0.2 and brings the specimen almost into an optimum-doped state.

Fig. 6 is a diagram showing relationships between T_c of a specimen in the first form of embodiment of the invention annealed, its normally conducting electrical resistivity, carrier density and weight's rate of change and the annealing temperature.

Referring to Fig. 6, annealing a specimen in an over-doped state causes oxygen to come out of it, resulting in a decreases in its carrier concentration and hence a rise in T_c . At the annealing temperature of 400°C, oxygen coming off radically brings the specimen into an under-doped state while maintaining T_c high.

A rise further in the annealing temperature further decreases the oxygen concentration, but is followed by a change in electronic state which increases the carrier concentration so it nears its optimum doping amount. And at the annealing temperature of 540°C, T_c becomes its maximum. And ye, at any temperature of 700°C or more, oxygen further coming off causes the specimen to deteriorate.

The phenomenon that a change in electronic state increases the carrier concentration has been mentioned before in connection with figs. 7 and 8, and can be explained as follows: To wit, Tl ions present in charge supply layers are trivalent (+3) and Tl_{6s} level lies above the Fermi level (E_F) if the oxygen concentration is high. As the oxygen concentration lowers, Tl ions are reduced to become monovalent (+1) and the Tl_{6s} level becomes lower than the Fermi level. This causes Tl ions to pull electrons out of the 5-coordination CuO₂ surface that is a superconducting layer and conversely to supply the superconducting, 5-coordination CuO₂ surface with holes.

In this manner, selective reduction of Tl ions can supply holes, thereby increasing the carrier concentration.

It should be noted at this point that from measurement of changes in the upper critical magnetic field, a selective reduction type

high temperature superconductor is found to have coherence length of 3 Å or more in c-axis. Also, from measurement of the ratio of the upper critical magnetic field in the c-axis to those in the a- and b-axes, its superconducting anisotropy is found to be 10 or less.

5 Mention is next made of a second, preferred form of embodiment of the invention.

10 This second form of embodiment is a thin film of a selective reduction type high temperature superconductor with $n = 3$ having a composition: $(Cu_{1-x}Tl_x)(Ba,Sr)_2Ca_2Cu_3O_y$ with the structure, like that of the afore-mentioned first form, as shown Fig. 2(a).

Continued, an explanation is given in respect of a method of making for the second form of embodiment.

First, a precursor component Cu-Ba-Ca-O has Tl_2O_3 uniformly mixed therewith in an amount of 0.25 to 0.5 mol to prepare:

15 $Cu_{1-x}Tl_xBa_2Ca_3Cu_4O_y$ where $x = 0.25$ to 0.5 ,

and by pressing to form thallium mixed pellets each of a diameter of 10 mm and a weight of about 450 mg.

Next, such a thallium mixed pellets is pre-heated for 1 hour to prepare a pellet for thallium adjustment.

20 Next, a $SrTiO_3$ substrate has an amorphous film of $(Cu_{1-x}Tl_x)(Ba,Sr)_2Ca_2Cu_3O_y$ built up thereon by RF magnetron sputtering using, for example, a sintered $TlBaSrCa_2Cu_3O_y$ body as a target.

25 Subsequently, the $SrTiO_3$ substrate having the amorphous film built up thereon, the thallium mixed pellet and the pellet for thallium adjustment are encapsulated in a capsule made of Au, Ag or Pt and then are heat-treated at a temperature of $860^\circ C$ to $890^\circ C$ for a period of 30 to 90 minutes to cause an epitaxy film of $(Cu_{1-x}Tl_x)(Ba,Sr)_2Ca_2Cu_3O_y$ to epitaxially grow from the amorphous film. This process will be referred to below as "amorphous phase epitaxy (APE) process".

30 The superconductor film of $(Cu_{1-x}Tl_x)(Ba,Sr)_2Ca_2Cu_3O_y$ obtained by the APE process is annealed in a low oxygen gaseous atmosphere of 1 atm or less at a temperature of $500^\circ C$ for a period of 30 minutes to

prepare a selective reduction type high temperature superconductor of the composition with $x = 0.4$ to 0.8 as the second form of embodiment of the invention.

It should be noted here that the method of making described above for the second form of embodiment is applicable to a (Cu, M) family, high temperature superconductor as well with the composition formula (c) mentioned in connection with the first form of embodiment of the invention. Here again as there, selective reduction can yield a positive hole dopable, high temperature superconductor.

The second form of embodiment of the invention is advantageous in that it gives rise to J_c that is so high as $J_c = 1 \times 10^6$ to 2×10^7 A/cm² (77K, 0T).

Fig. 9 is a diagram showing an X-ray analysis pattern of a specimen in the second form of the invention.

As shown in Fig. 9, a strong (001) peak is found, indicating that a c-axis orientation is the case. The c-axis here has a lattice constant of 15.89 Å that lies between 14.79 Å of a Cu-oxide high temperature superconductor and 15.93 Å of Tl-oxide high temperature superconductor.

Also, from observation of X-ray culminating (peak, extreme) points it has been confirmed that an in-plane orientation is the case ($\Delta \phi = 0.5$ to 1.5 degree).

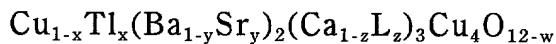
It has further been shown that the composition $(\text{Cu}_{0.5}\text{Tl}_{0.5})(\text{Ba},\text{Sr})_2\text{Ca}_2\text{Cu}_3\text{O}_y$ if annealed at a temperature of 870 to 900°C for a period of 30 to 90 minutes has $T_c = 95$ to 113 K and $J_c = 1 \times 10^6$ to 2×10^7 A/cm² (77K, 0T).

Mention is next made of a third, preferred form of the present invention. The selective reduction type high temperature superconductor in the third form of embodiment is a superconductor film of $n = 4$, the composition $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ having a structure as shown in Fig. 2(b). This structure as indicated in the Figure is referred to herein as Cu-1234.

An explanation is given in respect of a method of making a superconductor in the third form of embodiment of the invention.

A SrTiO_3 substrate has an amorphous film of $(\text{Cu}_{1-x}\text{Ti}_x)\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ built up thereon by RF magnetron sputtering using a sintered body composed of $\text{Cu}_{1-x}\text{Ti}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ as a target. The amorphous film, together with pellets as mentioned in connection with the second form of embodiment, in a capsule made of Au, Ag or Pt and then is heat-treated at a temperature of 880°C to 920°C for a period of 1 hour. Further, the heat-treated amorphous film after having an electrode film of Au deposited thereon is annealed in a low oxygen gaseous atmosphere of 1 atm or less at a temperature of 450 to 500°C for a period of 30 minutes to prepare a selective reduction type high temperature superconductor as the third form of embodiment of the invention.

The preceding method used to make a superconductor in the third form of embodiment is applicable to making a selective reduction type high temperature superconductor that can be indicated by composition formula (d):



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

An explanation is next given in respect of properties of a selective reduction type high temperature superconductor according to the third form of embodiment of the present invention.

X-ray analysis of the thin film shows that it has a lattice constant of 18.9 to 18.5 Å that lies between 17.99 Å of Cu-1234 And 19.11 Å of Tl-1234.

The X-ray peak pattern has a half-width $\Delta \phi = 0.5$ to 1.5, indicating a good orientation in the a-b plane.

Further, from composition analysis by an energy distribution type composition analyzer (EDX), it has been found that $x = 0.4$ to 0.8

and from measurement of electrical resistivity T_c has been found to be 100 to 115 K. J_c has been found to lie between 1 and 2×10^6 A/cm². Improving the preparation process may further rise both T_c and J_c .

While a method of making a selective reduction type high temperature superconductor according to the present invention permits changing n by its preparation composition or the preparation composition of the target material, it should be noted that the n can be changed by changing the reaction temperature and the treatment time period as well. A selective reduction type high temperature superconductor of optimum properties has currently been found to be obtainable with n of 4 to 6 and a thickness of unit lattice $(CaCuO_2)_n$ of 10 to 16 Å.

Although the present invention has hereinbefore been set forth with respect to certain illustrative forms of embodiments thereof, it will readily be appreciated to be obvious to a person skilled in the art that many alternations thereof, omissions therefrom and additions thereto can be made without departing from the essences of scope of the present invention. Accordingly, it should be understood that the invention is not intended to be limited to the specific forms of embodiment thereof set forth below, but to include all possible forms of embodiment thereof that can be made within the scope with respect to the features specifically set forth in the appended claims and encompasses all the equivalents thereof.

Industrial Applicability

As has been set forth in the foregoing description, a selective reduction type high temperature superconductor and a method of making the same according to the present invention are extremely useful in the superconducting electronics industry that involves large scale superconducting power transmission, superconducting power storage or reserve, superconducting electronic components such as a high performance Josephson device, a high frequency device or the like.

What is claimed is :

1. A selective reduction type high temperature superconductor characterized in that the high temperature superconductor has a portion 5 of its constituent elements selectively reduced whereby it has a superconducting layer thereof doped with positive holes.

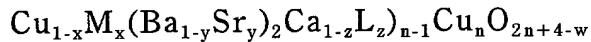
2. A selective reduction type high temperature superconductor as set forth in claim 1, characterized in that said high temperature 10 superconductor has a portion of its constituent elements selectively reduced whereby there are formed in superconducting layers a first and a second region doped overly and doped optimally with superconducting carriers, respectively.

15 3. A selective reduction type high temperature superconductor as set forth in claim 1 or claim 2, characterized in that said high temperature superconductor has a portion of its constituent elements selectively reduced whereby the superconductor as a whole has a superconducting carrier concentration such that it is held doped overly 20 or doped optimally with superconducting carriers.

4. A selective reduction type high temperature superconductor as set forth in claim 1, claim 2 or claim 3, characterized in that said superconductor has on each of an upper and a lower surface of a unit cell 25 thereof a charge supply layer having each of a portion of Cu atoms substituted with a selectively reducible atom.

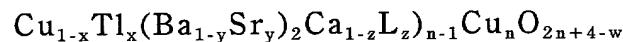
30 5. A selective reduction type high temperature superconductor as set forth in claim 1, claim 2 or claim 3, characterized in that said superconducting layers have an upper and a lower surface constituted by a CuO_2 surface of 5-coordination and a surface other than the upper and lower constituted by a CuO_2 surface of 4-coordination.

6. A selective reduction type high temperature superconductor as set forth in claim 1, claim 2 or claim 3, characterized in that it is made of a (Cu, M) family high temperature superconducting material that can
5 be described by composition formula:



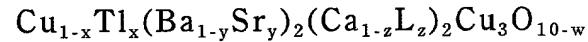
where M represents ions of one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os; L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.
10

7. A selective reduction type high temperature superconductor as set forth in claim 1, claim 2 or claim 3, characterized in that it is made of a (Cu, Tl) family high temperature superconducting material that can be described by composition formula:
15



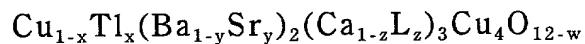
20 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

8. A selective reduction type high temperature superconductor as set forth in claim 1, claim 2 or claim 3, characterized in that it is made of a (Cu, Tl) family high temperature superconducting material that can be described by composition formula:
25



30 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

9. A selective reduction type high temperature superconductor as set forth in claim 1, claim 2 or claim 3, characterized in that it is made of a high temperature 5 superconducting material that can be described by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.
10

10. A selective reduction type high temperature superconductor as set forth in any one of claims 1 to 9, characterized in that the concentration of superconducting carriers is adjusted by 15 selective reduction or by varying (increasing or decreasing) oxygen concentration.

11. A selective reduction type high temperature superconductor as set forth in claim 6, characterized in that it is a 20 selectively over-doped type or a selectively optimum-doped type, high temperature superconductor in which n is any one of 3, 4, 5, 6 and 7.

12. A selective reduction type high temperature 25 superconductor as set forth in any one of claims 1 to 11, characterized in that selective reduction causes said substitutional ions in a said charge supply layer to receive electrons in their outer shell orbits, thereby providing holes in the CuO_2 surface of 5-coordination of a said superconducting layer.

30

13. A selective reduction type high temperature superconductor as set forth in any one of claims 1 to 12, characterized

in that it has a superconducting anisotropy of not greater than 10, and a coherence distance of not less than 3 angstroms.

14. A selective reduction type high temperature superconductor as set forth in any one of claims 1 to 13, characterized in that said selective reduction transforms its natural superconducting wave function that is of a d-wave to a wave function of a $(d + is)$ wave that has also a property of an s-wave.

10 15. A method of making a selective reduction type high temperature superconductor, characterized in that it comprises the steps of:

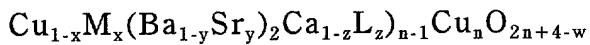
preparing a high temperature superconductor, and
heat-treating the prepared high temperature superconductor in
15 a reducing atmosphere.

16. A method of making a selective reduction type high temperature superconductor, comprising the steps of:

20 using an amorphous film as a precursor of high temperature superconductor;
causing the amorphous film to grow epitaxially by amorphous phase epitaxy; and
heat-treating in a low oxygen, reducing atmosphere the amorphous film that has grown epitaxially.

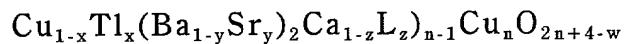
25 17. A method of making a selective reduction type high temperature superconductor, comprising the steps of:
causing added constituent elements to develop their self-forming effect; and
30 causing the high temperature superconductor to grow epitaxially by the self-forming effect.

18. A method of making a selective reduction type high temperature superconductor as set forth in any one of claims 15 to 18, characterized in that it is applicable to making a (Cu, M) family selective reduction type high temperature superconductor expressed by
5 composition formula:



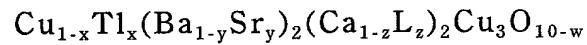
where M represents ions of one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os; L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.
10

19. A method of making a selective reduction type high temperature superconductor as set forth in any one of claims 15 to 17, characterized in that it is applicable to making a (Cu, Tl) family selective reduction type high temperature superconductor expressed by composition formula:



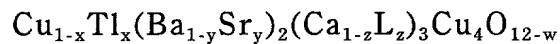
20 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; $0 \leq w \leq 4$; and $1 \leq n \leq 16$.

25 20. A method of making a selective reduction type high temperature superconductor as set forth in any one of claims 15 to 17, characterized in that it is applicable to making a (Cu, Tl) family selective reduction type high temperature superconductor expressed by composition formula:



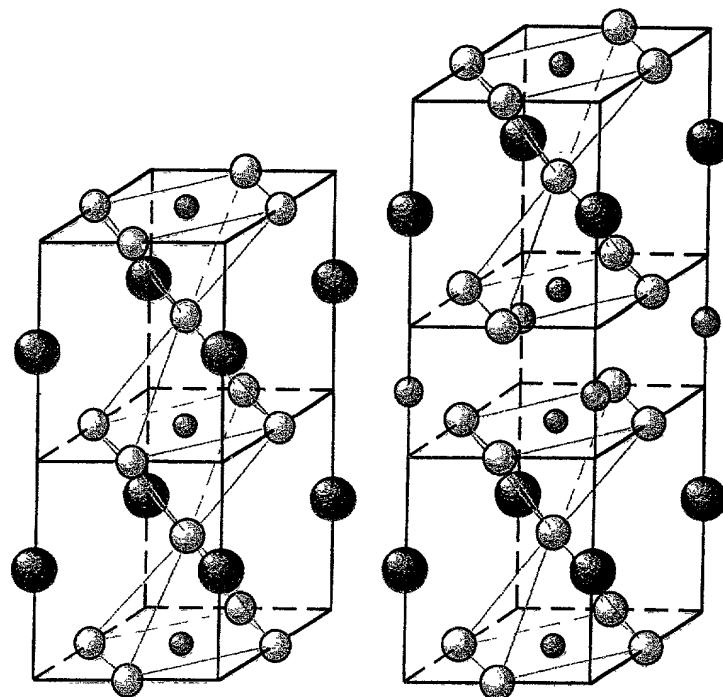
30 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.

21. A method of making a selective reduction type high temperature superconductor as set forth in any one of claims 15 to 17, characterized in that it is applicable to making a selective reduction 5 type high temperature superconductor expressed by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements; $0 \leq x \leq 1.0$; $0 \leq y \leq 1$; $0 \leq z \leq 1$; and $0 \leq w \leq 4$.
10

Cu O Ca Ba
Tl



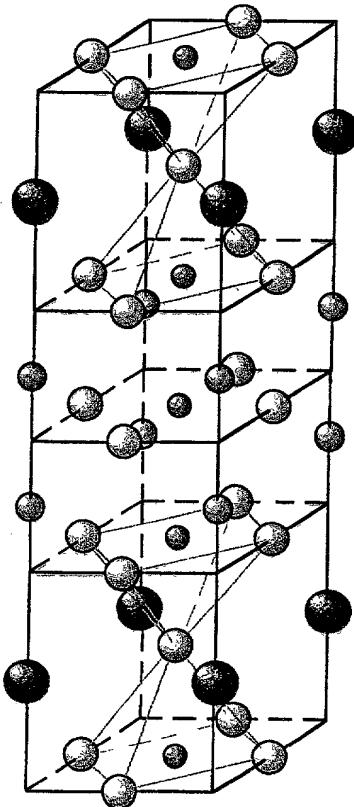
Cu-1201

Cu-1212

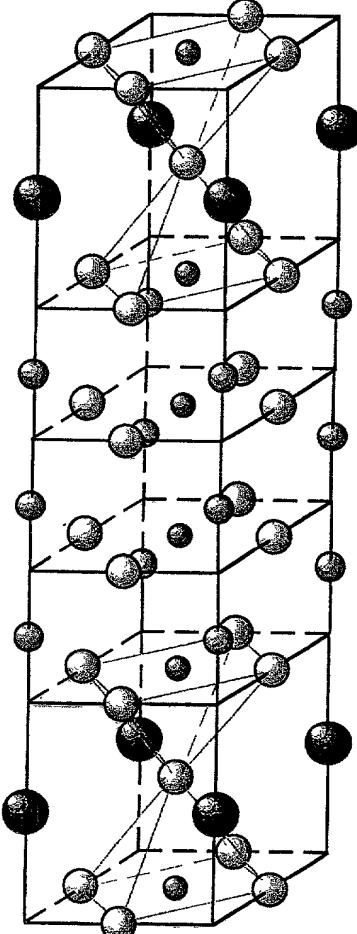
FIG. 1A

FIG. 1B

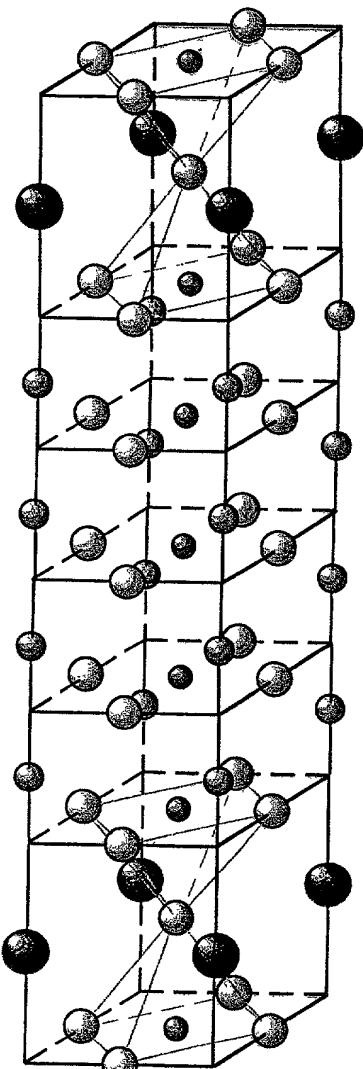
Cu O Ca Ba



Cu-1223



Cu-1234

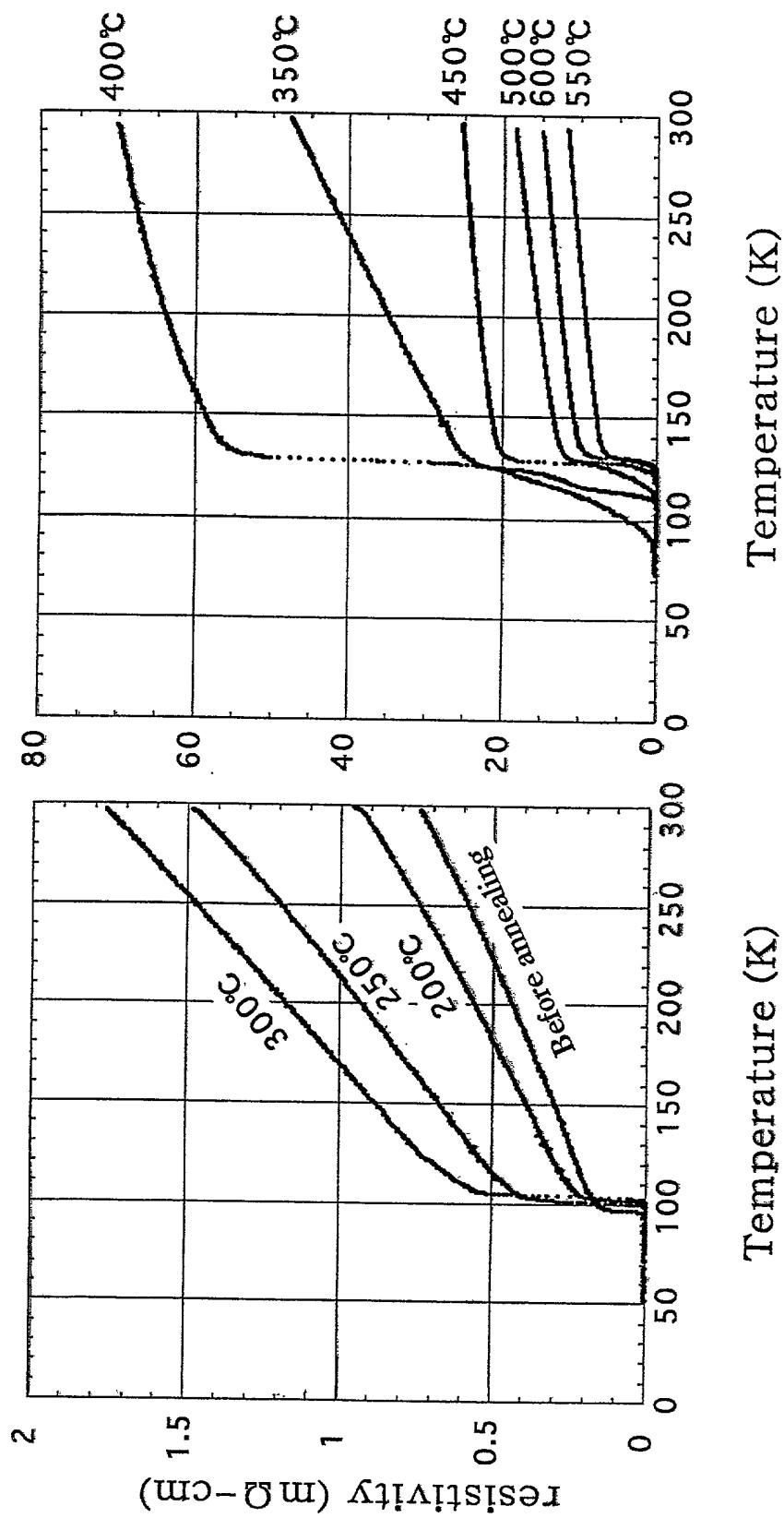


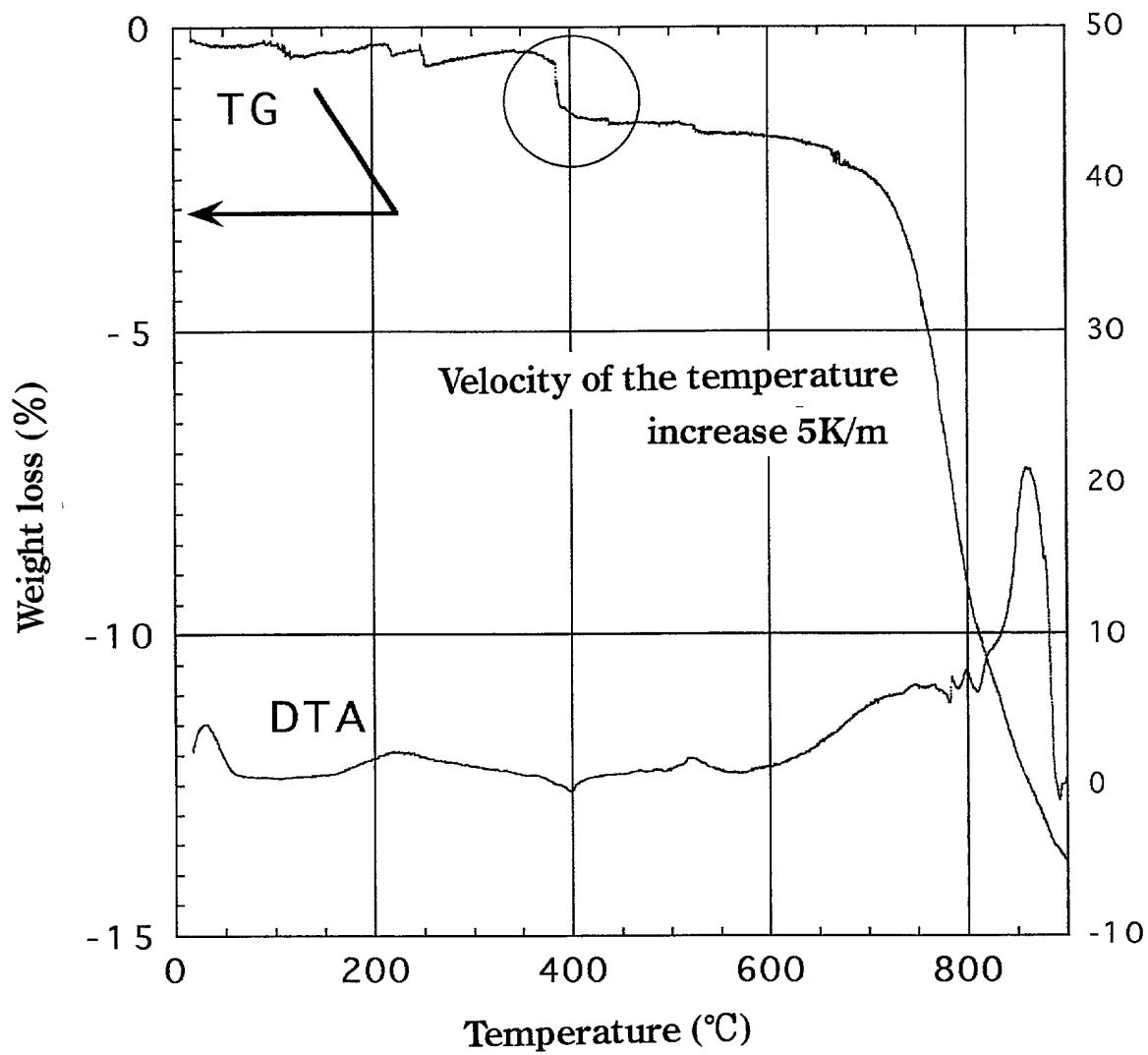
Cu-1245

FIG. 2A

FIG. 2B

FIG. 2C





Differential thermal analysis of (Cu, Tl)-1223

FIG. 4

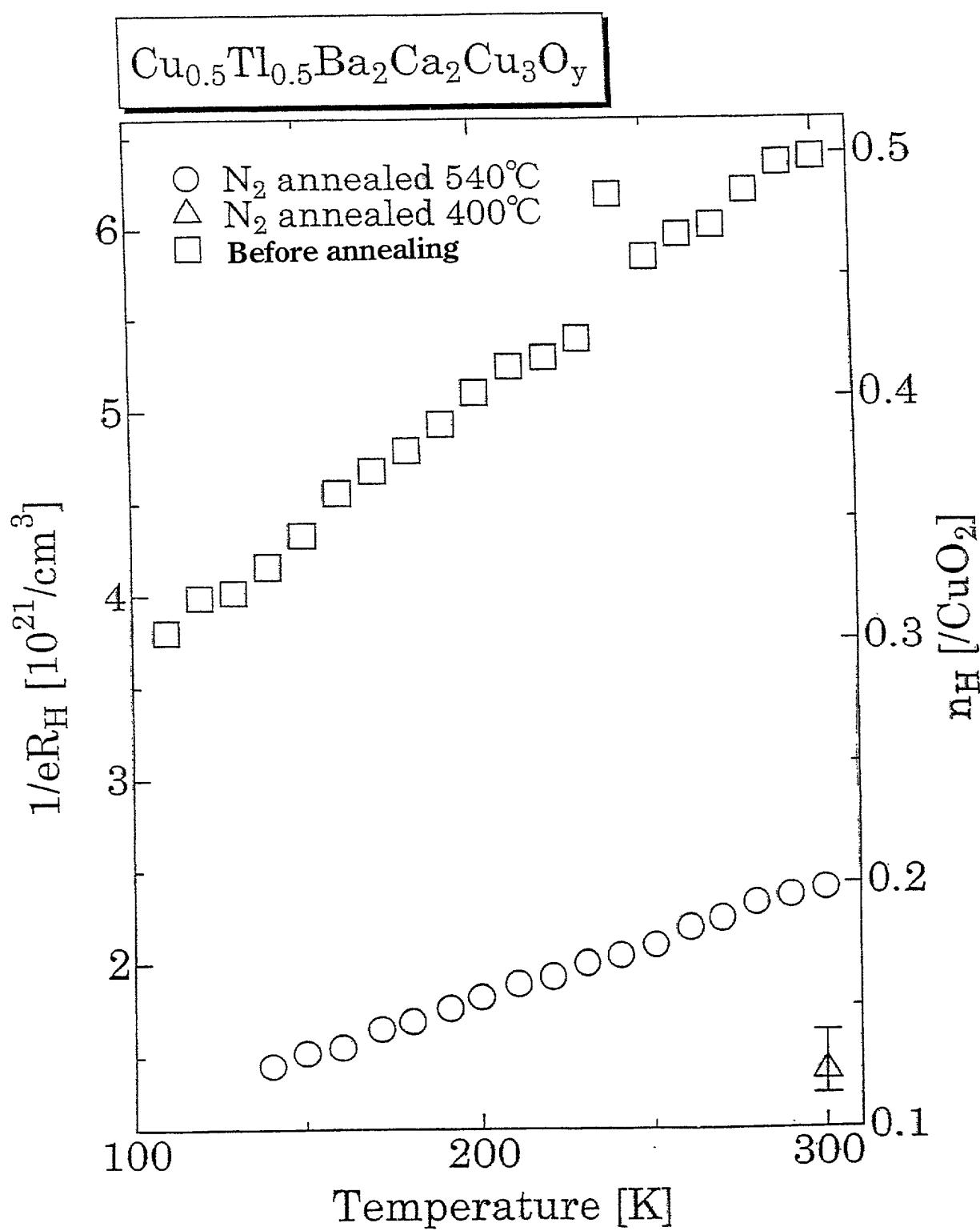


FIG. 5 Hole concentration for Cu found from measurement of Hall coefficient

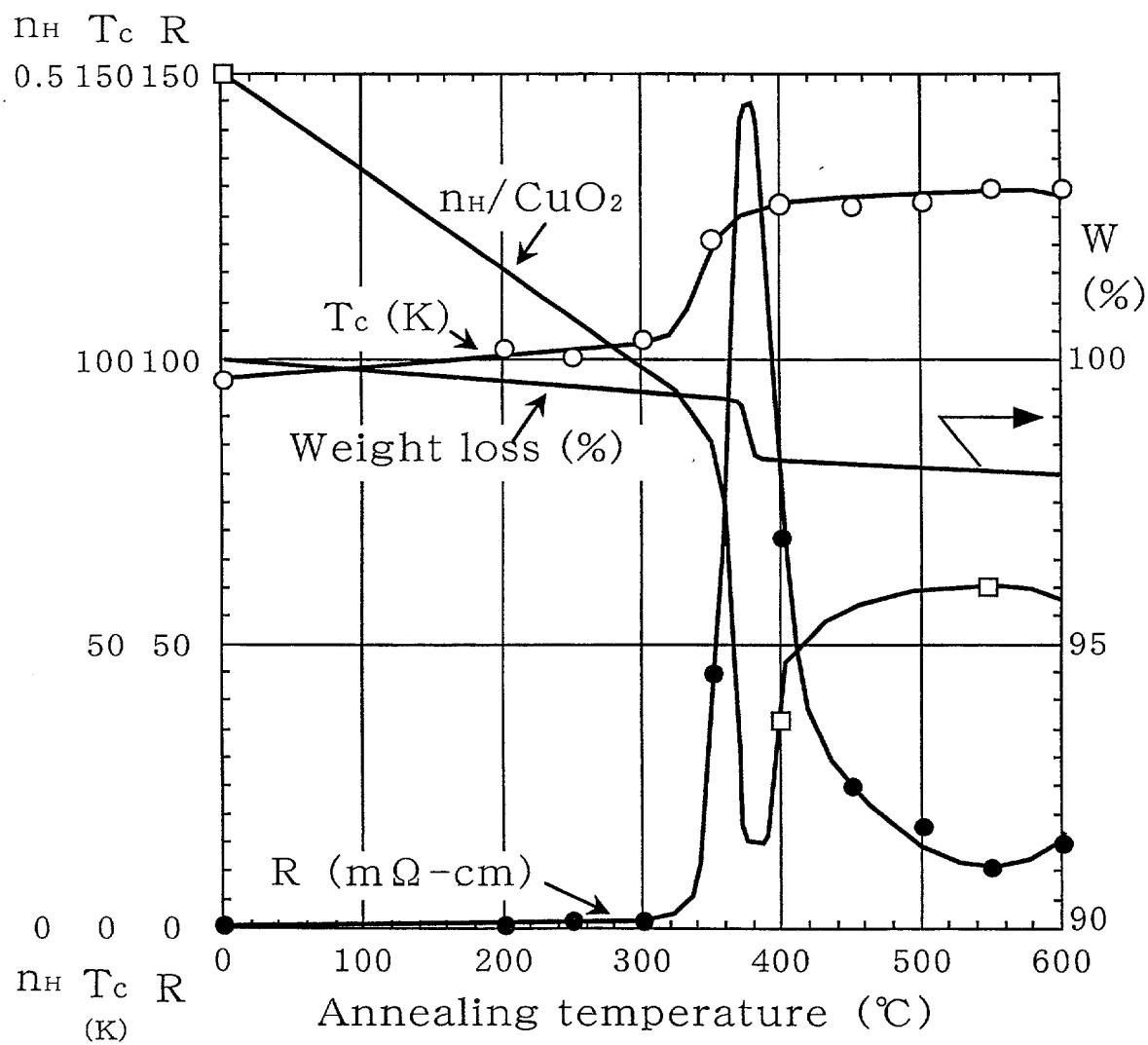


FIG. 6

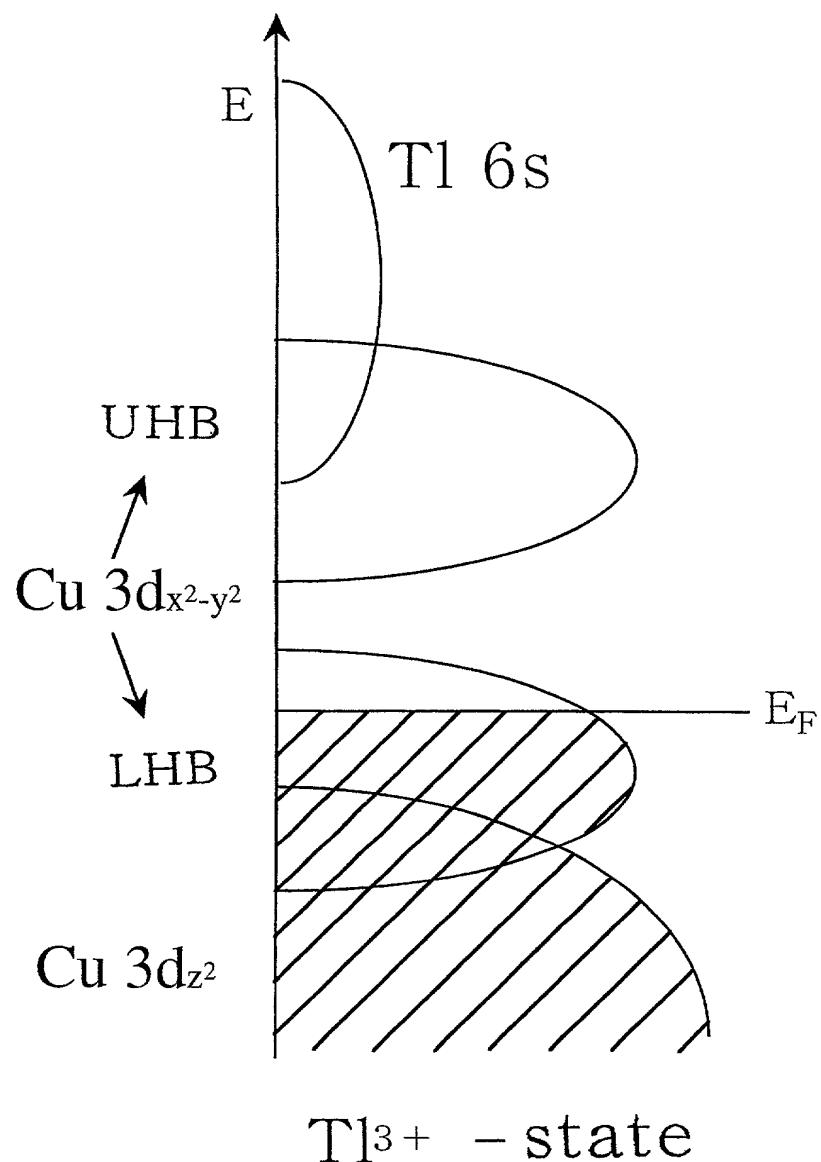


FIG. 7

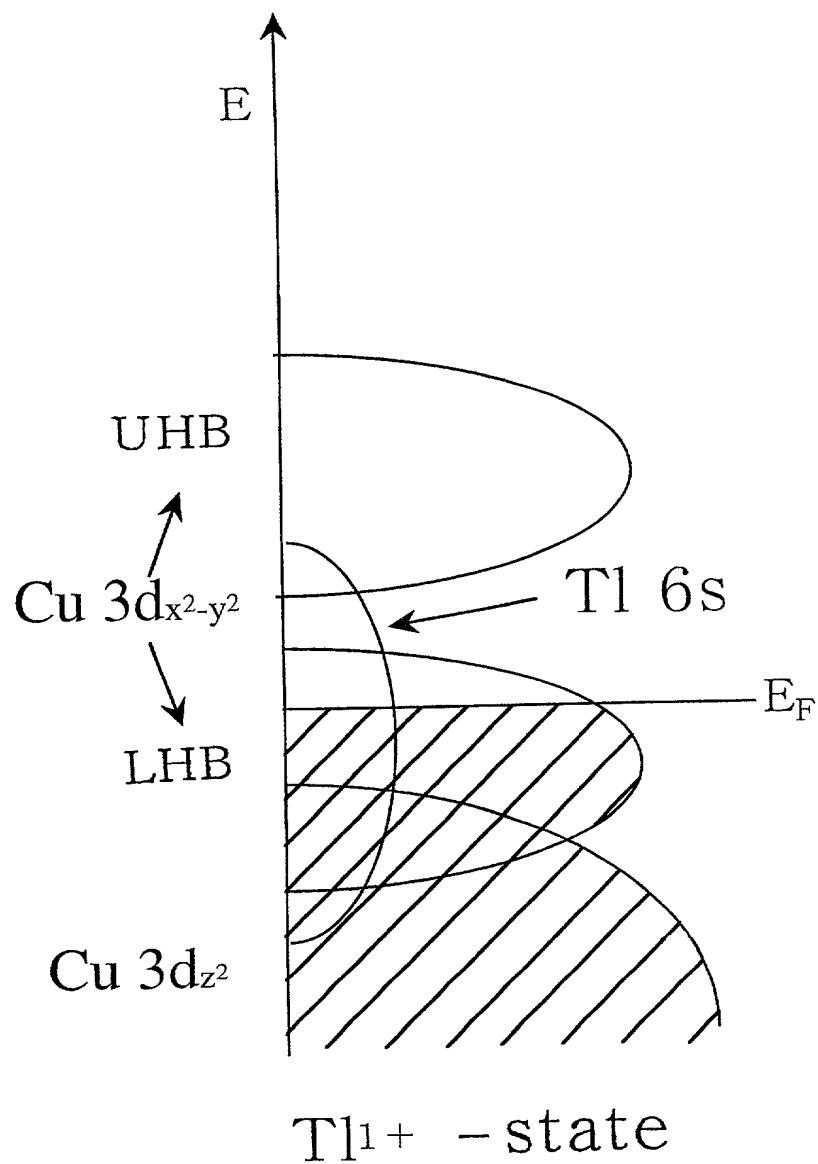


FIG. 8

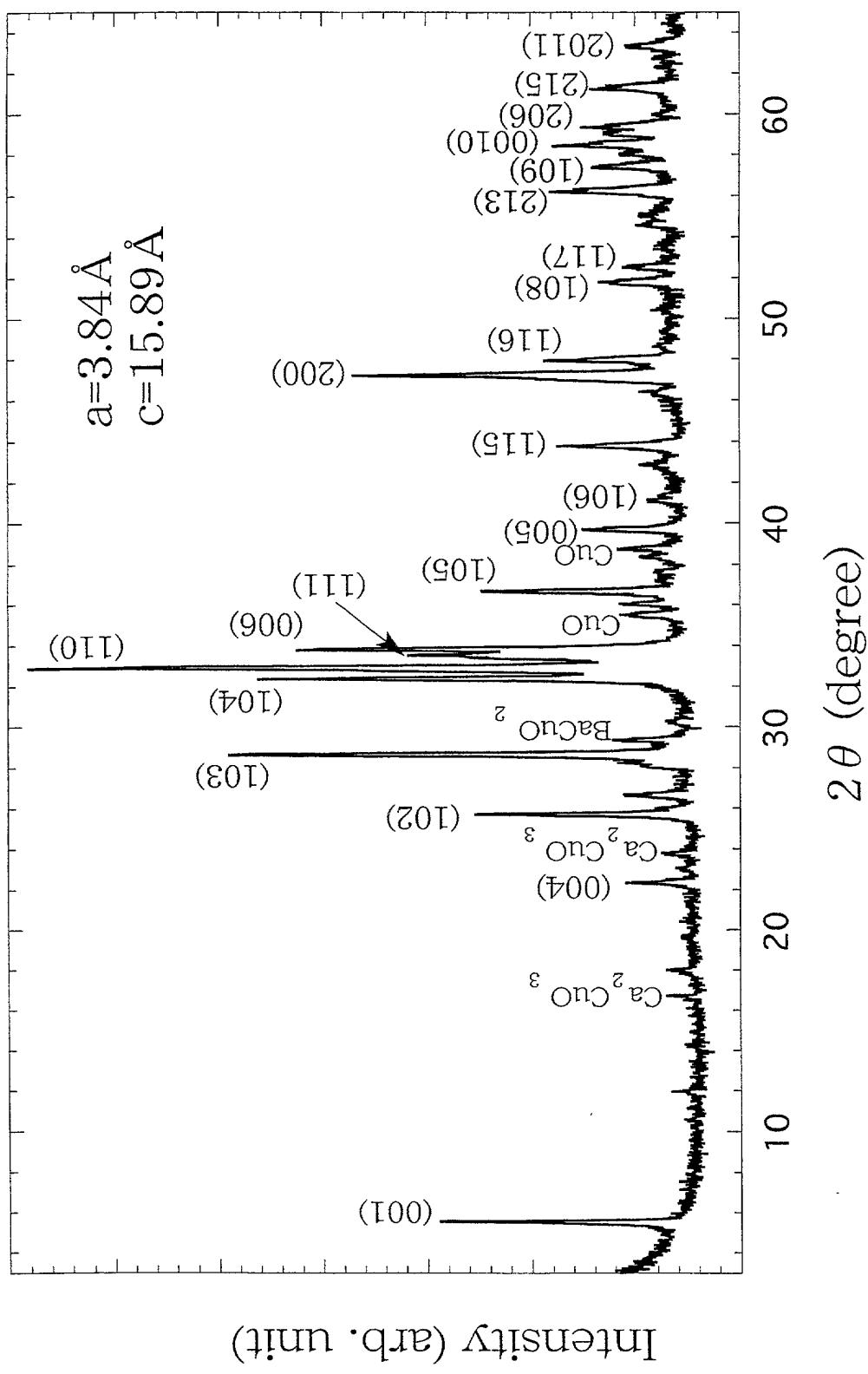


FIG. 9

(Cu,Tl)-1223 XRD

Declaration For U.S. Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention **entitled**
 (Insert Title) SELECTIVE REDUCTION TYPE HIGH TEMPERATURE SUPERCONDUCTOR AND
METHODS OF MAKING THE SAME

the specification of which is attached hereto unless the following is checked:

was filed on March 17, 2000 as United States Application Number or PCT International Application Number PCT/JP00/01669 and was amended on _____

(if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

List prior foreign applications. See note A on back of this page	1999-85003	Japan	26/03/1999	Priority Claimed
	(Number)	(Country)	(Day/Month/Year Filed)	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
	(Number)	(Country)	(Day/Month/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No
	(Number)	(Country)	(Day/Month/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No
	(Number)	(Country)	(Day/Month/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No

(See note B on back of this page)

See attached list for additional prior foreign applications

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of the application:

List Prior U.S. Applications	(Application Serial Number)	(Filing Date)	(Status) (patented, pending, abandoned)
	(Application Serial Number)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

James E. Armstrong, III, Reg. No. 18,366; William F. Westerman, Reg. No. 29,988; Ken-Ichi Hattori, Reg. No. 32,861; Le-Nhung McLeland, Reg. No. 31,541; Ronald F. Naughton, Reg. No. 24,616; John R. Pegan, Reg. No. 18,069; William G. Kratz, Jr., Reg. No. 22,631; Albert Tockman, Reg. No. 19,722; Mel R. Quintos, Reg. No. 31,898; Donald W. Hanson, Reg. No. 27,133; Stephen G. Adrian, Reg. No. 32,878; William L. Brooks, Reg. No. 34,129; John F. Carney, Reg. No. 20,276; Edward F. Welsh, Reg. No. 22,455; Patrick D. Muir, Reg. No. 37,403; Gay A. Spahn, Reg. No. 34,978; John P. Kong, Reg. No. 40,054; and Luke A. Kilyk, Reg. No. 33,251.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18 of the United States Code, § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor (given name, family name) Hideo, IHARA

(See note
C above)

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Inventor's Signature _____ Date _____

Residence _____ Citizenship _____

Post Office Address _____

Full name of third inventor (given name, family name) _____

Inventor's Signature _____ Date _____

Residence _____ Citizenship _____

Post Office Address _____

Full name of fourth inventor (given name, family name) _____

Inventor's Signature _____ Date _____

Residence _____ Citizenship _____

Post Office Address _____

Full name of fifth inventor (given name, family name) _____

Inventor's Signature _____ Date _____

Residence _____ Citizenship _____

Post Office Address _____

Full name of sixth inventor (given name, family name) _____

Inventor's Signature _____ Date _____

Residence _____ Citizenship _____

Post Office Address _____

Full name of seventh inventor (given name, family name) _____

Inventor's Signature _____ Date _____

Residence _____ Citizenship _____

Post Office Address _____

Full name of eighth inventor (given name, family name) _____

Inventor's Signature _____ Date _____

Residence _____ Citizenship _____

Post Office Address _____